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13. ABSTRACT *(Maximum 200 words)*

A mathematical model to simulate the low and high pressure crystal growth processes has been developed. The model accounts for both the melt and gas flows induced by buoyancy and capillary forces and by crystal and crucible rotations, radiation heat transfer from the melt and crystal surfaces, and the effect of the magnetic field. An efficient numerical scheme based on multizone adaptive grid generation and curvilinear finite volume flux discretization has been implemented to predict the interface shape and dynamics accurately. The effectiveness of the computer model (MASTRAPP) in solving phase change transport processes with deformable boundaries and moving interfaces has been demonstrated by performing simulations for a wide range of parameters for "one-step" in-situ synthesis and growth of indium phosphide crystals, a process being developed by the USAF Rome Laboratory. An innovative approach of coupled finite volume-finite element algorithm has also been developed to calculate the stresses in the growing crystal. Numerical results show a complex thermal interaction between the gas and the melt flows, and also indicate that the temperature fluctuations can be suppressed by the application of a magnetic field.

14. SUBJECT TERMS

Czochralski growth, high pressure crystal growth, LEC growth, MLEK growth, indium phosphide crystal growth, process modeling.

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Final Report

MODELING AND DESIGN OF HIGH PRESSURE CRYSTAL GROWTH PROCESSES

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Background. Many of the inhomogenities and defects in the crystal grown from a pool of melt are a direct result of the non-steady nature of the growth kinetics and complex heat transfer and flow mechanisms. The Czochralski process to grow III-V compound crystals such as indium phosphide and gallium arsenide, is much more complex than that for the silicon. It requires that the melt be covered by an encapsulant and the furnace be maintained at a high pressure to prohibit the separation of the volatile component from the melt. The presence of the gas and an encapsulant layer in a liquid-encapsulated Czochralski (LEC) or liquid-encapsulated Kyropoulos (LEK) process change the heat exchange pattern into the furnace as well as the interface and meniscus conditions and growth dynamics, compared to that in a CZ Si process. In such systems, the melt flow is oscillatory and the recirculatory inert gas flow is turbulent. It is therefore important to understand and analyze the mechanisms of energy transport and interaction between the gas and melt flows in moderate and high pressure crystal growth (HPCG) system which involve all modes of heat transfer, radiation, conduction and convection, and varying flow regimes. However, very little is known on thermal characteristics of these systems.

In addition, there is a strong desire to develop a "one-step" in-situ synthesis and growth process in order to reduce the growth cost and eliminate the possibility of contamination that are inherent to the conventional growth of compound crystals. In such processes, the polycrystalline compound ingots are produced in a synthesis chamber and the growth is carried out later in a separate HPCG system. Although "one-step" in-situ synthesis and growth is now commercially successful for gallium arsenide, a similar process for InP crystals is still under development at the USAF Rome Laboratory. In addition to developing a basic understanding of the physical phenomena underlying the high pressure synthesis and growth, this research is also aimed at helping the Rome Lab researchers in making the proposed process successful. Several additional issues such as reaction rate for synthesis, stoichiometry and chemical equilibrium need to be considered to carry out a successful synthesis.

Computational Scheme. To overcome the difficulties associated with time-varying domains and irregular boundaries, many different kinds of algorithms have been proposed based on the choice of (a) the numerical method, e.g., finite element, finite difference and finite volume, and (b) the selection of the mesh system, e.g., fixed and moving grid fields. Several commercial and non-commercial software are now available that can simulate these kinds of processes. Most of these computer models are based on finite element methods primarily because they are inherently suitable for complex geometries as well as for the stress calculations.

To simulate the transport phenomena associated with moderate and high pressure crystal growth, we have developed a high resolution computer model, MASTRAPP, based

on the finite volume scheme, that is specially suitable for multiphase, multicomponent transport systems. The numerical scheme employs (a) a multizone adaptive grid generation (MAGG) for the discretization of the physical domains of arbitrary shapes by using an adaptive optimization of the grid characteristics, and (b) a curvilinear finite volume (CFV) scheme for the discretization of the governing equations. In the area of multizone adaptive finite volume algorithm it concentrates on the development of an efficient algorithm for clustering of grids in the interface regions as the solutions progress, for problems involving irregular domains and free as well as moving boundaries and interfaces. A generalized set of two-dimensional governing equations for the entire multiphase crystal growth system has been derived in curvilinear coordinate system, and transformation relations for coefficients and equations for moving interfaces have been obtained. An efficient numerical scheme based on finite volume flux discretization, non-staggered grids, power law for convective fluxes, and pressure correction formulation has been implemented. The model incorporates both melt and gas flows induced by buoyancy and capillary forces and by crystal and crucible rotations, as well as the radiation heat transfer from the melt and crystal surfaces. The MAGG technique is much more efficient and has better characteristics for phase change and free surface problems than the methods commonly used, particularly by the commercial packages. The scheme allows smoothness and orthogonality in the vicinity of the internal interfaces, and has proved to be very powerful and robust for thermal and flow interactions at the melt/solid, melt/gas and solid/gas interfaces. This is primarily because the equations for direct and dynamic link between the zonal and interfacial grid generation have been developed based on a constrained variational optimal method. Since it uses a TDMA solver for the CFV, the memory requirement is small and the solution process is fast. The solution adaptivity further makes the solution procedure efficient and more accurate.

Using MASTRAPP2d, it has been possible to investigate the high pressure synthesis and growth for a wide range of parameters and interesting effects of melt/gas thermal interaction are demonstrated. The high pressure growth is governed by a large number of parameters such as Grashof and Prandtl numbers for the melt and gas flows; crystal and crucible Reynolds numbers; Biot number for radiation heat transfer; Froude and Bond numbers for surface tension; density, viscosity, thermal conductivity and specific heat ratios for solid and melt phases; thermophysical property variation in the gas; geometric variables, and so on. These parameters vary greatly with a change in phase/zone, as well as with the surface conditions. Suitable values of these numbers need to be selected to perform realistic simulations. A major difficulty in calculating the relevant values of governing parameters in many cases is a lack of precise information on thermophysical properties as well as the variation in furnace configurations. However, preliminary calculations based on estimated values of process parameters have provided a great insight into the problem.

Magnetic Field Effects. Since the electronic materials such as Si, GaAs and InP, behave as liquid metals, an externally applied field can suppress the temperature and flow oscillations and thereby can stabilize the growth process. A magentohydrodynaimc model is therefore developed to study the effects of magnetic field on MCZ and MLEK growth. The model can allow to examine the conditions under which a magnetic field can be

helpful, and demonstrate the physical effects on the melt flow and interface shape and dynamics.

Stress Calculations. Thermal stress is considered to be the primary source of dislocations in the growing crystal. The problem becomes much more severe as the diameter of the crystal is increased and/or when III-V compound crystals are grown. It is believed that a knowledge of thermal stress as a function of process parameters can help in understanding and improving the pulling process. We have implemented an innovative approach of coupling the finite-volume transport solutions with the finite element stress calculations to predict stresses in the crystal based on the evolving interface shape and the temperature distribution in the crystal. This FVM-FEM coupled scheme is very efficient due to its inherent adaptivity to the grid generation and control element. No iterations between the FVM solutions and FEM calculations are required. This coupled method has been fully tested. The new scheme is accurate and efficient and also easy to implement.

Simulations and Results. The growth of III-V compound crystals with a focus on InP has been simulated by the MASTRAPP2d (a) to demonstrate the effectiveness of the MAGG scheme to simulate multiphase systems with more than one material, and free and moving interfaces; and (b) to show the complexity of the flow structure and temperature field in a HPCG system. It is found that a portion of the crystal may be heated by convection from the hot crucible wall while the other portion of the crystal is cooled by convection losses to the cold walls. The radiation and conduction models, that neglect convection in the gas and have been widely used in the literature, are not valid for the HPCG growth. The convective heat transfer also plays a key role in setting up the interface and boundary conditions. The temperature distribution on the surface boundary is usually determined by both the convective and radiative heat transfer. Cooling on the top of the crystal also has a significant effect on the temperature distribution in the crystal, the shape and dynamics of the crystal/melt interface, and the pulling velocity. As the crystal is grown, the flow pattern as well as the shape of the crystal/melt interface are changed drastically. In the case of a small crystal, the convective heat transfer has a stronger influence due to a large volume of the gas and a short distance between the top surface of the crystal and the crystal/melt interface. On the other hand, the side wall boundary condition plays an important role in determining the crystal/melt interface and temperature distribution in the crystal when the crystal is long. Calculations presented thus far only preliminary but they serve the purpose of demonstrating the strong effects gas convection can have on the high pressure growth.

The stress calculations indicate that accurate predictions of thermal stresses are possible only if the melt convection is included in the model. (Most of the stress models for CZ growth neglect melt flows.) The results indicate that in the case of high pressure growth the gas convection significantly affects the stress field by modifying the temperature distribution in the crystal.

Various stages of the "one-step" in-situ synthesis for indium phosphide melt have also been simulated for the first time. However, calculations presented here are only preliminary and are not ready to be compared with the experimental data at this time due to lack of information on boundary conditions and process variables, as well as since the

phosphorus vaporization and exothermic reaction have been neglected by the model. The results, however, indicate that the synthesis conditions in a HPCG system are extremely complex. The quartz shield is very useful in isolating the strong convective flows in regions close to the cold wall from the buoyant flow directly above the melt, and to reduce the intensity of the gas flow along the seed shaft. The buoyancy dominated flow pattern in the system changes significantly with the rotation of the crucible and heat shield. It stabilizes the gas flow and increases the heat transfer between the injector bottom and gas flows. The positions of the seed and injector also affect the thermal field in the furnace dramatically. As the injector moves downward, the temperature of the injector bottom increases which is helpful for the synthesis. Since the injector temperature is controlled by an energy balance between radiation and convection heat transfer and vaporization of phosphorus, the model needs further improvement. Simulation of this kind can provide a better understanding of the HPCG process and can help the process designer to develop a process or redesign the system to achieve improved synthesis and growth conditions.

The details of the mathematical model, numerical scheme, code development and simulation results can be found in the following publications.

Grant Related Publications

Prasad, V., and Zhang, H., 1995, "Challenging Issues in Bulk Crystal Growth Modeling," Invited paper, Proc. American Ceramic Society Annual Meeting, Cincinnati.

Prasad, V., Bliss, D. F., and Adamski, J.A., 1995, "Thermal Characterization of the High Pressure Crystal Growth System for In-Situ Synthesis and Growth of InP Crystals," *Journal of Crystal Growth*, Vol. 142, pp 21-30.

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Zhang, H., Prasad, V. and Moallemi, M.K., 1995, "A Numerical Algorithm Using Multizone Adaptive Grid Generation for Multiphase Transport Processes with Moving and Free Boundaries," *Numerical Heat Transfer* (submitted).

Zhang, H., Prasad, V., and Bliss, D.F., 1995, "Transport Phenomena in a High Pressure Crystal Growth System: In-situ Synthesis for InP Melt," *Journal of Crystal Growth* (submitted).

Zhang, H., Prasad, V., and Bliss, D.F., 1995, "Transport Phenomena in High Pressure Crystal Growth Systems for III-V Compounds," *Journal of Crystal Growth* (submitted).

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Zhang, H., and Prasad, V., 1995, "Multizone Adaptive Simulations for High Pressure Crystal growth," Proc., *ASME/JSME Thermal Engineering Joint Conference*, Maui, Hawaii, pp. 559-568.

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Zhang, H., and Prasad, V., 1994, "A Novel Computational Scheme for Phase Change Materials Processing," *Materials Research Society* FAll Meeting, Boston.

Zhang, H., Prasad, V., and Glimm, J., 1994, "Modeling of Transport Phenomena in a High Pressure Crystal Growth System," *AFOSR Computational and Physical Mathematics Contractors Meeting*, Albuquerque.

Zhang, H., Prasad, V., and Glimm, J., 1995, "A Magnetohydrodynamic Model for Crystal Growth Processes," *AFOSR Computational and Physical Mathematics Contractors Meeting*, Albuquerque.

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Interactions

The research team had active collaboration with the crystal growth researchers at USAF Rome Laboratory, Hanscom AFB, MA. Regular visits were made and discussions to interlink the experimental research at Rome Laboratory and numerical work at Stony Brook continued throughout the grant period

GT Equipment Technologies in Nashua, NH received a Small Business Technology Transfer Research (STTR) award on "Modeling Simulation and Design of High Pressure Crystal Growth Systems" in the partnership with SUNY at Stony Brook. The research from this AFOSR grant helped in Phase I efforts of the technology transfer.